Boron Nitride-Aluminum Nitride (BAN) Interfaces and Coatings and Methods for their Production and Use

Field of the Invention

Interface compositions comprising boron-aluminum-nitride and methods for coating ceramic fibers such as SiC with a boron-aluminum-nitride nanocomposite coating for use in ceramic matrix composites are provided. Such matrices are useful in high temperature applications and in oxidizing atmospheres such as in the aerospace industry and jet engine industry.

Background of the Invention

The performance of ceramic matrix composites (CMC) depends greatly on the interaction between the composite components at mutual interfaces (Singh, R.N. J. Am. Ceram. Soc. 1989 72:1764-1767; Hull, D. An Introduction to Composite Materials, Cambridge Univ. Press, Cambridge, UK, 1981; Pirouz et al. Importance of Interfacial Strength on Fracture Toughness of Brittle Matrix Composites, Surfaces and Interfaces of Ceramic Materials, 1.-C. Dufour et al. (eds.), 737-760, 1989). Long and short fibers, whiskers, platelets and coarse equiaxial particles are used as reinforcement in composites, with long, continuous fibers improving mechanical properties most efficiently.

The most vulnerable component of SiC_f/SiC and other similar CMC systems, however, is the interface that separates the fiber and the matrix. If cracks exist in a composite in an oxidizing environment at an elevated temperature, the interface is exposed to the environment. To maintain the debonding and sliding properties that are required for good mechanical properties, either the interphase must be resistant to oxidation or the composite system must protect the interphase from oxidation. It is most desirable for the interphase to be an oxidation-resistant material; however, to date, no such interphase has proven effective at high temperatures for the SiC_f/SiC system. For non-oxide composite systems such as SiC/SiC composites, a single oxide interphase material has not been demonstrated, to date, to exhibit the weak interface behavior while being sufficiently compatible with the fiber and matrix materials at high temperatures.

Although both the matrix and fiber components of older SiC/(Si/SiC) composites generally exhibit acceptably high resistance to oxidation, these composites become increasingly vulnerable to oxidation and consequent embrittlement whenever mechanical

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or thermomechanical loads become large enough to crack the matrices. Even the narrowest cracks become pathways for the diffusion of oxygen. Typically, to impact toughness to an SiC/(Si/SiC) composite, the SiC fibers are coated with a material that yields at high stress to allow some slippage between the fibers and matrix. If oxygen infiltrates through the

5   cracks to the fiber coating, then, at high temperature, the oxygen reacts with the coatings (and eventually with the fibers), causing removal of the interphase, undesired local bonding between fibers and the matrix and consequent loss of toughness. In addition, the resultant concentration of stress and deterioration of the fibers at the bonding locations give rise to failure of fibers. If the process of oxidation continues, then eventually the

10   remaining fibers become unable to bear the load, causing the composite to fail at a stress appreciably below its initial (as-fabricated) ultimate strength.

Non-oxide ceramic systems of silicon carbide and silicon nitride are used as ceramic matrix materials of structural composites intended for high temperature service. These non-oxide ceramic systems combine excellent mechanical, chemical, thermal and

15   physical properties. In particular, SiC matrices have utility in high temperature applications. For example, single phase refractory SiC ceramics are widely used at temperatures above 1500°C (Boecker, W.D.G., Ceram. Forum Int./ Ber. 1997 74:244-251).

Oxide ceramic matrices used in industry typically comprise alumina and/or mullite.

20   These non-oxide and oxide ceramic matrices are used in continuous ceramic fiber reinforced composites for gas turbine applications. Matrices used in this application need to have properties including high stiffness at low and high temperatures, high strength, high thermal and mechanical stability, high oxidation and corrosion resistance, small diameter for CMC fabricability and low cost for commercial viability.

25   The most commonly used non-oxide coatings for ceramic fibers are carbon and boron nitride (U.S. Patent 4,642,271; Singh, R.N. and Brun, M.K. Adv. Ceram. Mater. 1988 3:235-37; Cao et al. J. Am. Ceram. Soc. 1990 73(6):1691-99; Morscher et al. Ceram. Eng. Sci. Proc. 1997 18:7-8; and Moore et al. J. Am. Ceram. Soc. 1997 80(5):1285-1288). Carbon is the most widely used material for coatings because it is generally less

30   expensive. The carbon coating must form a compliant layer that mitigates the effect of thermal stress: a thicker carbon coating reduces the thermal stresses better than a thinner coating (Kerans, R.J. Control of Fiber-Matrix Interface Properties in Ceramic Matrix Composites, pp. 301-12 in Proceedings of High Temperature Ceramic Matrix Composites.

Edited by R. Naslain, J. Lamon, and D. Doumeingts. Woodhead Publishing Limited, France, 1994). However, carbon is easily accessible to oxygen at high temperatures (Halblg et al. Oxygen Diffusion and Reaction Kinetics in Continuous Fiber Ceramic Matrix, Annual Cocoa Beach Conference and Exposition on Composites, *Advanced*

5   *Ceramics, Materials and Structures*, Jan 20-24, 1998). Accordingly, carbon-rich interfaces, produced either by natural fiber/matrix reaction (for NICALON or TYRANNO within silicate matrices) by solution method or by vapor deposition on fiber precursors (such as in CVI SiC/SiC composites), present a low temperature (~400°C) limit in oxidizing environments (air, combustion products). In these CMCs, flash oxidation

10   pretreatment of either the matrix itself or the fiber ends is used to prevent channeled carbon oxidation and provide protection from oxidation, but only in the absence of matrix microcracking (Pluckett et al. J. Mater. Sci. Lett. 1995 14:1223). However, matrix cracking always occurs under cyclic oxidation conditions and this method does not work for long-term high-temperature applications of composites.

15   Boron nitride has also been suggested as a potential fiber coating in SiC/SiC composites for high temperature application. A boron nitride coating allows the debonding of SiC fibers in reinforced SiC matrix composites. A process was recently developed to produce a boron nitride rich region on the surface of Nextel 312 fibers (Campbell, S.S. and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 327-336; Campbell, S.S.

20   and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 337-343). The process is accomplished by heating the boria containing fibers to high temperatures in an atmosphere containing ammonia. The resulting BN-rich region is not an external, distinct coating, but rather a thin (about 100A) region integral to the individual filaments (Sikonia, J. Nitrided Nextel 312 Fiber, IWG Workshop, 10-11 June 1997, WPAFB, OH 97).

25   However, BN is not stable in oxidizing environments and forms a liquid oxide B_2O_3 above 450°C. The presence of B_2O_3 leads to a series of synergistic reactions. For example, it can enhance SiO_2 formation from SiC. The SiO_2 and B_2O_3 can then react to form stable borosilicates such as SiO_2-B_2O_3, which is eutectic at 372°C (Roth et al. Phase Diagrams for Ceramists, VI, Am. Ceram. Soc., Westerville, OH, 1969, p. 156). This

30   situation occurs in a composite when the BN fiber coating has ready access to oxygen. These reactions lead to fiber consumption and degradation of fiber properties as well as fiber/matrix bonding, which then degrades the mechanical properties of the composites at elevated temperatures (Henager, C.H. and Jones J. Cer. Eng. Sci. Proceedings 1992 13(7-

8):411-19). Thus, while BN has improved oxidation resistance over carbon coatings, there are many stability problems associated with its use, especially at intermediate temperatures and in the presence of water vapor (Petrak, D.R. CMC Interface Studies at Dow Corning, IWG Workshop, 10-11 June 1997, WPAFB, OH; Morscher et al. Ceram.

5   Eng. Sci. Proc. 1997 18:7-8; More et al. The Stability of BN-containing CMCs Exposed to Oxygen and Water Vapor in the Temperature Range 425-1150°C, Abstract of the 193 Meeting of the Electro-Chemical Society, Abstract 812, 98-1, San Diego, 1998). These stability issues of BN are related to several factors, including BN crystallographic structure, extent of crystallization, interface reactions, and impurity content, especially

10   oxygen (Ailey et al. Stability of BN Interfacial Coating During Oxidation and Exposure to Water Vapor, Annual Cocoa Beach Conference and Exposition on Composites, Advanced Ceramics, Materials and Structures, Jan 20-24, 1998; More et al. The Stability of Various BN Interfacial Coating in SiC/SiC Composites Exposed to Oxygen and Water Vapor in the Temperature Range 425-950°C, IWG Workshop, WPAFB, OH, 10-11 June 1997). In

15   particular, water vapor that is always present in significant amounts in combustion environments results in a very fast removal of the interfacial layer. The BN phase is very sensitive even to small amounts of water vapor in the oxidizing gas stream. This sensitivity is due to formation of highly stable $H_xB_yO_z$ (g) species from the reaction of water vapor and B_2O_3. A low processing temperature BN fiber coating volatilizes readily

20   in the presence of water vapor (Morscher et al. Ceram. Eng. Sci. Proc. 1997 18:7-8). Less volatilization occurs with BN materials are processed at high temperatures and/or doped with silicon. An examination of BN coated SiC fibers in a SiC matrix illustrates recession of BN in water vapor containing environments. This process is described with gas phase transport of $H_xB_yO_z$ (g) out of pores in the SiC matrix.

25   In addition, no inexpensive methods exist for production of low-cost BN coatings on SiC fibers. Further, no methods exist for production of these coatings without bridging the fibers in the tow or fabric.

       Thus, the use of non-oxide CMCs in high temperature structural applications is presently limited by the environmental instability exhibited by conventional interphase

30   materials such as C and BN fiber coatings.

       Strategies currently used for oxide/oxide systems have attempted to replicate some of the microstructural features of the above-described nonoxides using phases with a low-cohesion layer-plane to form an oriented crystal interface by *in-situ* reaction between a

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simple fiber coating and surrounding matrix (U.S. Patent 5,137,852; Cinibulk, M.K. Ceram. Eng. Sci. Proc. 1994 15(5):721-28; and Lee et al. J. Am. Ceram. Soc. 1998 81(3):717-20). An empirical search for complex oxides having a high probability of low cohesion with a matrix or fiber due to polarization of oxygen bonds by high valence
5   cations, exemplified by vanadates, phosphates or niobates of type ABO_4, has also been performed. A large number of ABO_4 compounds such as tungstates, molybdates, tantalates and niobates are also being considered as fiber coatings for oxide-oxide systems (Goettler et al. Ceram. Eng. Sci. Proc. 1997 18(3):279-286). Due to its easy cleaving basal planes, potassium calcium niobate ($KCa_2Nb_3O_{10}$) perovskite oxide has also been investigated as
10   an interfacial coating material for oxide/oxide composites (Kim et al. Cleaving Oxides – KCN, IWG Workshop, 10-11 June 1997, WPAFB, OH).

Kerans (Control of Fiber-Matrix Interface Properties in Ceramic Matrix Composites, pp. 301-12 in Proceedings of High Temperature Ceramic Matrix Composites. Edited by R. Naslain, J. Lamon, and D. Doumeingts. Woodhead Publishing Limited,
15   France, 1994) provides a review of some of the oxide interface concepts and interphase materials that have been considered for oxide composite systems. These include porous oxides, damaged oxides, easy-cleaving oxides, ductile interphases and segregant weakened interfaces. However, experimental results are relatively scarce in terms of validating the usefulness of these interface concepts.

20   Use of a monazite ($LaPO_4$) coating in oxide-oxide compositions was recently disclosed (Kuo et al. J. Am. Ceram. Soc. 1997 80(12):2987-96). This oxide fiber, when used in an oxide matrix, circumvents the problem of high temperature oxidation (Kuo et al. J. Am. Ceram. Soc. 1997 80(12):2987-96). The $LaPO_4$ coating material provides a high-temperature oxide-constituent composite with an inherently weak interface (U.S.
25   Patent 5,514,474). However, coating of oxide fibers with monazite can be problematic. A higher specific weight of oxide composites in comparison with silicon carbide CMCs is also disadvantageous for aerospace applications. Any oxide coating on a nonoxide fiber and/or in a nonoxide matrix creates a thermodynamically unstable system that will degrade in the process of high-temperature manufacturing of the composite.

30   Accordingly, there is a need for improved ceramic matrix composites less vulnerable to oxidation and consequent embrittlement when mechanical and thermodynamic loads become large enough to crack the matrices.

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Summary of the Invention

An object of the present invention is to provide an interface composition or coating for ceramic fibers of ceramic matrix composites, said interface composition or coating comprising boron-aluminum-nitride.

5   Another object of the present invention is to provide a ceramic matrix composite comprising ceramic fibers coated with boron-aluminum nitride.

Another object of the present invention it to provide methods for production of a ceramic matrix composite comprising ceramic fibers coated with boron-aluminum-nitride.

10   ## Brief Description of the Figures

Figures 1(a), 1(b) and 1(c) show the oxidation of carbon, boron nitride and boron-aluminum nitride (BAN) interphases, respectively.

Figure 2 shows the thermodynamical calculation in a BN-AlN system of the present invention.

15   Figure 3 shows a phase diagram of an Al_2O_3-B_2O_3 system of the present invention.

Detailed Description of the Invention

The most vulnerable component of the ceramic matrix composites is the interphase that separates the fiber and the matrix. It is most desirable for the interphase to be an

20   oxidation-resistant material. However, available interphases for CMC systems such as the SiC_f/CMC have proven ineffective at high temperatures. There is no fiber coating currently available that can provide protection to the fiber and maintain it's debond characteristics for the desired life (1000 hours).

The present invention provides a new interface composition comprising boron-

25   aluminum-nitride (BAN) and methods for production of the interface composition via coating ceramic fibers with a boron-aluminum-nitride (BAN) nanocomposite coating. The BAN coating of the present invention provides oxidation protection for long-fiber reinforced CMCs because it forms refractory aluminum borates upon oxidation, including $Al_{18}B_4O_{33}$, which is stable till >1900°C and provides a diffusion barrier, and a boria-

30   containing liquid phase (B_2O_3 at low temperatures or B-Al-O and/or B-Al-Si-O at higher temperatures), which seals cracks in the matrix or along the fiber/matrix interface. The composite with a BAN interface is expected to resist oxidation for 1000 hours over the temperature range from 400 to 1200°C and possibly at higher temperatures. The coating

can be obtained using a cost-saving, high temperature chemistry technique easily scaled up for mass production. BAN coatings are compatible with a majority of ceramic fibers and provide fiber debonding and pullout similar to BN. Unlike pure BN, however, BAN is robust and provides oxidation protection in a flow of combustion products. While the

5   oxide coating cannot provide a gettering action to the oxygen, the advantage of this nonoxide coating is that it provides this gettering action while it is oxidizing, thus preventing the oxidation of the underlying fiber. Therefore, from an oxidation standpoint, this nonoxide coating is expected to be better than oxide coatings.

Examples of ceramic fibers of commercial and experimental interest for high

10   temperature aerospace applications which can be coated in accordance with the present invention include, but are not limited to, silicon carbide based fibers such as Nippon Carbon's Hi-NICALON (β–SiC with excess carbon and low oxygen content; Zhang, Z.F. Processing Silicon Carbide Fibers from Organosilicon Precursors, Ph.D. Dissertation. The University of Michigan, Ann Arbor, MI 1994; Strife et al. Cer. Eng. Sci. Proc. 1990 11(7-

15   8):871-919; Okamura et al. Proc. 1st Jap. Int. SAMPE Symp. 1989 929-934; Takeda et al. Ceram. Eng. Sci. Proc. 1993 14(9-10):540-547; Takeda et al. Ceram. Eng. Sci. Proc. 1994 15:133-141; Chollon et al. Structure, Composition and Mechanical Behavior at High Temperature of the Oxygen-Free Hi Nicalon Fiber, High Temperature Ceramic Matrix Composites II, Eds. Evans, A.G., Naslain, R., American Ceramic Society, Westerville,

20   OH, 299-304, 1995) and Ube's TYRANNO fibers (Yajima, S. J. Mater. Sci. 1981 16:1349-55; Yajima, S. Am. Ceram. Soc. Bull. 1983 62(8):893-98), "Hi-Nicalon S" fibers (Takeda et al. Ceram. Eng. Sci. Proc. 1996 4:35-42), powder derived and sintered α-SiC fibers from Carborundum (Venkateswaran et al. Development of Continuously Sintered Polycrystalline SiC Fiber, Proceedings of 17th Annual Conf. on Composites, Materials and

25   Structures, Cocoa Beach, FL 1993; Pysher et al. High Temperature Properties of Carborundum α-SiC Fibers, HITEMP REVIEW 1992, NASA Conf. Pub. 10104, 1, 22-1-12 1992), Zr-containing TYRANNO fibers (Kumagawa et al. Cer. Eng. Sci. Proc. 1997 18(3):113-118) and a polymer derived and sintered nearly stoichiometric polycrystalline fiber SYLRAMIC from Dow Corning (DiCarlo, J.A., Dutta, S., Continuous Ceramic

30   Fibers for Ceramic Composites. Handbook on Continuous Fiber Reinforced Ceramic Matrix Composites, eds Lehman R., El-Rahaiby S., Wachtman J., Ceramic Information Analysis Center, Purdue University, West Lafaette, Indiana, 1995). Fibers of these ceramic matrices are expected to be useful in the reinforcement of CMC's in 1000°C to

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1400°C temperature range. Other important fibers include the single phase Si-B-(N,C) fibers of Bayer AG (Baldus et al. Trans. Tech. Publ., CMMC 96, Eds Fuentes M., Martinez-Espanaola J.M., Daniel A.M., 177-183, 1996) , Textron's SCS-6 fibers and other fibers produced by the chemical vapor deposition on a carbon core.

5   In a preferred embodiment, the ceramic fibers used in the present invention comprise SiC, as SiC fibers are particularly useful for composites working at temperatures greater than or equal to 1200°C. However, boron carbide, boron carbonitride, silicon carbonitride and other carbide-containing fibers can be used. Chopped fibers, short fibers (whiskers) or nanofibers (nanotubes) can be coated in a similar way to continuous fibers or

10   fabrics.

          BAN material for coating of the ceramic fibers can be obtained as a geterophase composition comprising either a mixture of boron nitride and aluminum nitride or boron nitride and solid solution of BN-AlN structure of AlN. Plate-like crystals of boron nitride in such compositions ensure a low friction coefficient and easy sliding. High thermal

15   conductivity and low thermal expansion result in a high thermal shock resistance of BN-AlN ceramics. For example, when BN-Si_3N_4 composites survived 40 cycles 20-2500°C, BN-glass up to 78, than BN-AlN survived 98 (Dubovik, T.V., Methods of Formation, Properties and Application of Nitrides, Kiev, ONTI, IPMS, Academy of Science of USSR, 381, 197). Therefore, it is expected that BAN composition will provide debonding of

20   fibers, improve thermal shock resistance of composites and serve properly as a weak interphase between a ceramic fiber such as SiC_f and the matrix.

          Oxidation of boron and aluminum containing ceramics leads to formation of aluminum borates via alumina and boria. The aluminum borates provide a self-healing coating which arrests cracks and prevents oxidation of the fibers in the range from 450 to

25   greater than 1950°C so that there is no degradation of the fiber strength and no recession of the fiber-matrix interphase (see Figure 1). In the case of alumina forming materials, interaction of alumina with B_2O_3 results in the formation of stable refractory aluminum borates $2Al_2O_3 \cdot B_2O_3$ and $3Al_2O_3 \cdot 4B_2O_3$ and prevents the loss of B_2O_3 due to its vaporization (Schneider et al. Key Engineering Materials 1996 113:49-58; Gogotsi et al. J.

30   Mater. Sci. Lett. 1992 11:308-311). Further, it has been shown shows that liquid B_2O_3 can seal cracks in the oxide scale and improve oxidation resistance of boron-containing ceramics at very high temperatures (Gogotsi et al. J. Mater. Sci. Lett. 1992 11:308-311). AlN and boron compounds are also believed to be useful for oxidation protection of C/C

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and C/SiC composites as coatings containing AlN and boron compounds have been disclosed to form self-healing oxide scales (Courtois et al. J. Phys. III 1993 3(C2):843-853; Gogotsi et al. Key Engineering Materials 1997 132-1 36:1600-1603).

5   In the present invention BAN is used as an interphase in a CMC such as a SiCf/CMC thus preventing high temperature oxidation of the interphase while retaining good debonding properties of BN. The thermodynamical calculation depicted in Figure 2 shows direct evidence that AlN will decompose in the first turn, thereby preventing BN from further oxidation and creating self-healing protective compounds of aluminum borates.

10   The oxidation protection mechanism of the BAN interface of the present invention is based primarily on the crack sealing concept. The protection mechanism can be understood from the analysis of the phase diagram of Al_2O_3-B_2O_3 system (see Figure 3) and chemical reactions of BN and AlN with oxygen. Upon heating in air or combustion products, boron oxide is formed. Since its oxidation starts above 450°C, it first forms a

15   liquid phase.

From purely thermodynamic considerations, liquid boron oxide can react either with AlN or with Al_2O_3. However, the formation of the two borates is favored in case of the reaction between boron oxide and alumina.

The free energy of formation of $Al_4B_2O_9$ (Equation {2}) is 12 kJ/mol in

20   comparison with 471 kJ/mol in the case of oxygen presence (Equation {3}).

$$AlN + \tfrac{3}{4}\, O_2 \rightarrow \tfrac{1}{2}Al_2O_3 + \tfrac{1}{2}N_2 \qquad\qquad \Delta_rG^0_{(1200°K)} = -1295 \text{ kJ/mol} \qquad \{1\}$$

$$\tfrac{1}{2}Al_2O_3 + \tfrac{1}{4}\, B_2O_3 \rightarrow \tfrac{1}{4}Al_4B_2O_9 \qquad\qquad \Delta_rG^0_{(1200°K)} = -12 \text{ kJ/mol} \qquad \{2\}$$

$$AlN + \tfrac{1}{4}\, B_2O_3 + \tfrac{3}{4}\, O_2 \rightarrow \tfrac{1}{4}Al_4B_2O_9 + \tfrac{1}{2}N_2 \qquad \Delta_rG^0_{(1200°K)} = -471 \text{ kJ/mol} \qquad \{3\}$$
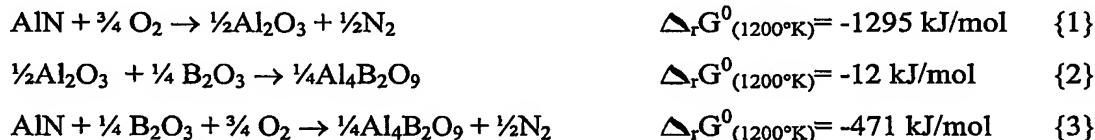
25   The free energy change in formation of $Al_{18}B_4O_{33}$ from oxides (Equations {4} and {5}) is -10 kJ/mol in comparison with the -469 kJ/mol for the interaction with AlN (Equation {5}).

$$\tfrac{1}{2}Al_2O_3 + 1/9\, B_2O_3 \rightarrow 1/18\, Al_{18}B_4O_{33} \qquad\qquad \Delta_rG^0_{(1200°K)} = -10 \text{ kJ/mol} \qquad \{4\}$$

$$AlN + 1/9\, B_2O_3 + \tfrac{3}{4}\, O_2 \rightarrow 1/18\, Al_{18}B_4O_{33} + \tfrac{1}{2}N_2 \qquad \Delta_rG^0_{(1200°K)} = -469 \text{ kJ/mol} \qquad \{5\}$$
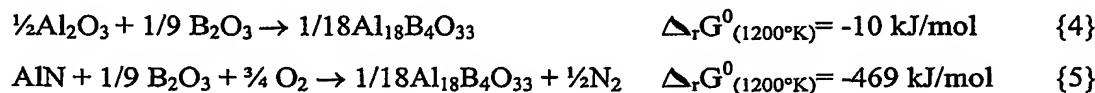
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The free energy changes of reactions depicted in Equations {2} and {4} on one hand, and reactions in Equations {3} and {5} on the other hand are very similar. Consequently, the

formation of both borates can occur with the same thermodynamic probability, depending on the local Al_2O_3/B_2O_3 ratio. As soon as B_2O_3 is formed, it reacts with AlN by the reaction depicted in Equation {3}, thus yielding $Al_4B_2O_9$ that forms a solid diffusion barrier at the BAN/liquid boria interface and provides a protective mechanism in the

5   temperature range of 450 to 1000°C. Accordingly, a typical protecting layer consisting of a solid phase (reaction, diffusion and erosion barrier) and a liquid phase (crack/pores sealant) forms from the very beginning of the oxidation. Thus, the composite is protected even at relatively low temperatures when low temperature degradation of composites with BN or carbon interphases unrelated to oxidation, also referred to as pesting, can occur

10   (Luthra, K.L. J. Am. Ceram. Soc. 1997 80(12):3253-57).

$Al_4B_2O_9$ melts above 1000°C (see Figure 3) releasing some boria and providing a second protective mechanism at temperatures exceeding 1000°C. Thus, if the composite is heated to temperatures above 1000-1050°C, the solid protective layer of $Al_4B_2O_9$ will become thinner, but it will not disappear. Instead, a very stable (melting point >1950°C)

15      $Al_{18}B_4O_{33}$ is formed which protects the BAN interphase at temperatures exceeding the working temperature of the fiber and of most matrices. For example, if the oxidation temperature is greater than 1150°C, or water vapor is present or erosion by the flow of combustion products occurs, pure BN interface disappears at a very high rate, unless protected by the oxidation products of the matrix. In the BAN interface of the present

20   invention, however, this will not happen even if an oxide matrix is used because a low activity of boria in $Al_{18}B_4O_{33}$ will keep B_2O_3 bonded and will prevent the degradation of the composite. In case of an oxidizable matrix (e.g. SiC or Si_3N_4), a protective aluminoborosilicate phase is formed that can supply additional protection due to the presence of a crack-sealing viscous silicate phase at temperatures above 1200°C.

25   Crystallization of mullite is possible from this phase at higher temperatures. Since aluminoborosilicate (Nextel 312) fibers work well in composites, also at high temperatures, it is believed that oxide layers with a similar composition will be compatible with most of composite matrices and stable up to very high temperatures.

Thus, it is believed that a BAN coating on a ceramic fiber, particularly SiC fibers,

30   provides an interface with appropriate mechanical properties and the oxidation resistance for utility in ceramic matrix composites. Composites comprising the BAN interface are expected to be useful in high temperature applications in oxidizing environments such as aerospace applications.

In a preferred embodiment, the BAN coating comprises AlN nanodispersed in BN. This nanodispersion improves oxidation resistance (comparable oxidation rate of AlN and BN and uniform propagation of the reaction front) and optimizes mechanical properties of the interface composition. This coating can also contain carbon or oxygen. Aluminum

5   oxide or oxynitride can be formed instead of AlN as these alternative aluminum-containing compounds produce the same protective borate layer upon oxidation. By the term "aluminum nitride" when used generally herein, it is also meant to be inclusive of these alternative aluminum-containing compounds.

Various methods are available for applying the BAN coating of the present

10   invention. In one embodiment, a method for synthesis of carbon coating on silicon carbide fibers by extraction of metal from carbide by either supercritical water or halogens and their compounds is used. This extraction method has been described in detail by Gogotsi et al. [(Key Engineering Materials 1997 132-136:1600-1603; Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW

15   "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998; J. Mater. Chem. 19197 7(9):1841-1848; Nature 1994 367:628-630; Hydrothermal Synthesis of Carbon Films on SiC Fibers and Particles, in H. Hausner, G.L. Messing and S.-I. Hirano (eds.), *Ceramic Processing Science and Technology*, Ceramic Transactions, Vol. 51, Am. Ceram. Soc., Westerville, OH, 243-247,

20   1995). An important feature of this method is that the carbon layer is not deposited on the surface, but rather the surface of SiC is transformed into carbon. Therefore, an extremely uniform coating with good adhesion is formed.

A schematical etching reaction leading to the formation of carbon on the surface of carbides can be written as follows:

25          $$MC \ (s) + D \ (g,l) = C \ (s) + M_yD_x \ (g,l) + D_z \ (g,l), \qquad \{6\}$$

where MC is a metal carbide, D is a gaseous or liquid etchant, M_yD_x is a gaseous or soluble etchant fragment species, and D_z is other possible etchant fragment species. Thermodynamic analysis shows that a number of compounds can act as etchants. In particular, supercritical water (Gogotsi et al. Formation of Carbon Coating on Carbide

30   Fibers and Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998) and halogens (Gogotsi et al. Key Engineering Materials 1997 132-136:1600-1603) have been predicted to extract metals from carbides under selected temperature, pressure

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and concentration conditions. Extraction of metals from carbides by halogens (F_2, Cl_2, Br_2 and I_2) or their compounds (HF, CCl_4, $CHCl_3$, etc.) can lead to the formation of free carbon. This method is more versatile than hydrothermal synthesis and it requires a relatively simple experimental setup.

5   Thermodynamic analysis of the reaction products in the system SiC/chlorine containing gases has been conducted in the temperature range 300-1300°C using a Gibbs energy minimization program. Thermodynamic simulation (Gogotsi et al. Formation of Carbon Coating on Carbide Fibers and Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and Fiber-Reinforced Composites", *Kluwer Academic*

10   *Publishers*, 217-230, 1998) demonstrated that carbon formation is expected with Cl_2 and other halogens. In the system of SiC/Cl_2, the reaction

$$SiC\ (g) + 2\ Cl_2\ (g) = SiCl_4\ (g) + C\ (s) \hspace{3cm} \{7\}$$

is most favorable thermodynamically, and at higher temperatures (above 900°C) the thermodynamic probability of the reaction

15     $$SiC\ (g) + 3/2\ Cl_2\ (g) = SiCl_3\ (g) + C\ (s) \hspace{3cm} \{8\}$$
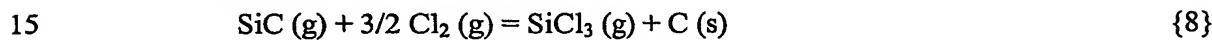
increases. Additionally, if oxygen impurities are present, SiO (g), CO (g), CO_2 (g) and SiO_2 (s) can be formed.

As a result of the above reactions, a carbon coating with uniform thickness and a disordered structure can be obtained. This coating is totally adherent to fibers and does not

20   form bridging between individual filaments in the fabric or tows. The thickness of layers depends on process conditions and can vary from several nanometers to several microns. Since the degree of porosity can be controlled by parameters of the treatment (see Table 1), materials with a specific adsorption capacity can be provided.

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Table 1. Specific surface area, S, and size of graphite crystallites, La, in SiC treated in Ar/Cl$_2$ and Cl$_2$/H$_2$ gases

Experimental conditions			Measured specific surface of SiC (m^2/g)	Carbon content (%)	Calculated surface area of carbon (m^2/g)	L$_a$ (nm), size of graphite crystallites
Gas	Temp. (°C)	Time (hrs)				
3.5% Cl$_2$/Ar	400	7	47.8	8	400	2.0 - 2.5
3.5% Cl$_2$/Ar	600	8	140.0	11	1163	2.4 - 2.6
3.5%Cl$_2$/Ar	1000	0	989.6	98	1010	2.0 - 4.5
2%Cl$_2$/2%H$_2$/Ar	1000	72	11.5	< 5 %	10	1.0 - 4.5
As-received SiC powder			13.6	< 3 %		2.0

Thin films of carbon can be obtained on SiC fibers or fabrics. Further, under selected
5   conditions, it is possible to obtain nanoporous carbon layers with very high specific area of
about 1000 m^2/g and pore size of 1 nm or less. These films allow for easy impregnation
with salts and a uniform nitride coating after nitridation.

Experiments with polymer derived (Tyranno) and CVD(SCS-6) fibers showed that
the formation of carbon is very uniform and does not change the shape of fibers. This is
10   indicative of the growth of carbon by extraction of Si from SiC and collapse of the cubic
structure of β-SiC to amorphous carbon. Raman spectra similar to that obtained from
hydrothermal amorphous carbon have been obtained from the carbon coatings on both
types of fibers (Gogotsi et al. Formation of Carbon Coating on Carbide Fibers and
Particles by Disproportionation Reactions, NATO ARW "Advanced Multilayered and
15   Fiber-Reinforced Composites", *Kluwer Academic Publishers*, 217-230, 1998). This leads
to the formation of a BAN nanocomposite material that is expected to have a higher
oxidation resistance compared to macro-structured BN/AlN.

Temperatures at about 400-700°C are required to obtain carbon coating by
chlorination. CVD fibers can be coated by chlorination at a lower temperature than is
20   required in the case of hydrothermal treatment. However, since CVD fibers do not degrade
at high-temperatures (up to 1500°C), temperatures as high as 1000-1100°C can be used to

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produce a carbon coating in a short time. Also, pre-existing carbon coatings on the fibers produced by CVD can be used in BAN synthesis.

Transformation of carbon to BAN is preferably performed using a commercially viable method such as that proposed for producing BN thin film on silicon carbide
5   whiskers using inexpensive borate precursors. The method is based on the reaction between boron and aluminum salts with carbon and ammonia upon heating. Three different BN precursors, sodium borate decahydrate ($Na_2B_4O_7$·$10H_2O$), ammonium borate tetrahydrate ((NH_4)$_2B_4O_7$·$4H_2O$), and boric oxide (B_2O_3) have been applied. $Al(NO_3)_3$·$9H_2O$ can be used to obtain AlN thin films on silicon carbide fibers (Brown, S.E.
10   and Partch, R.E. Abstracts of the 28th Annual Meeting of the Fine Particle Society, Dallas, Texas 1998). In these experiments, however, no uniform coatings were produced. The inability to produce uniform coatings was believed to result from samples being contaminated with sodium, which decreases the high-temperature strength and oxidation resistance of the fibers.

15   Thermodynamic analysis showed that B_2O_3 consumption starts at about 800°C and all boron oxide would be transformed to BN below 1200°C. Very similar results have been predicted for the formation of AlN. Due to a very fine (nanoporous) carbon coating, serious kinetic limitations of the reaction are not expected so that synthesis can be conducted at 1100-1200°C.

20   During the reactions, carbon layer absorbs the precursor melt, which further undergoes nitridation with ammonia at elevated temperatures. Carbon promotes the conversion of B_2O_3 and $Al(NO_3)_3$·$9H_2O$ to BAN and forms carbon monoxide as a byproduct. As the reaction progresses and BAN is formed, the porous carbon layer is completely or partly consumed resulting in a carbon-free or carbon-containing coating.
25   This can be controlled by changing the process parameters. Control of the ceramic coating thickness depends on the quantity and the physical characteristics of the carbon layer obtained by selective etching in halogens.

Nitridation was examined over a range of temperatures for varying amounts of time. Specifically, temperatures of 1100, 1200 and 1300°C for 10, 30, 60, 150 and 480
30   minutes each were examined. In each case BN was formed on the surface of all samples. The 10 minute reaction, in comparison to the 60 minute reaction, had less crystalline h–BN and a smaller crystalline size, suggesting that longer reaction times and nitridation temperatures may increase the quantity of crystalline h-BN.

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A similar chemical approach has been used by Allied Signal company to obtain BN coating on boron-containing alumina-silica (Nextel 312) fibers, which were thermally treated in the ammonia atmosphere (Campbell, S.S. and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 327-336; Campbell, S.S. and Gonszy, S.T. Ceram. Eng. Sci. Proc. 1994 337-

5   343). During this treatment, boria diffuses to the fiber surface and can be reacted with ammonia to form a thin BN coating on the surface. However, the required reaction temperature is higher than that of the $B_2O_3 + C + NH_3$ interaction and this process is not applicable to SiC fibers.

Thermodynamic calculation shows that synthesis of AlN from aluminum salts and

10   ammonia is feasible and that the suitable temperature for the reaction is approximately 700-900°C. Further, BN stays in equilibrium with AlN during the synthesis of AlN to produce a BN-AlN mixture on the carbon coated SiC first. AlN is produced after BN.

A suitable content of AlN (or AlON) in BN for the C-SiC coating is in the range of about 40-400%. At lower temperature (<1000°C), the product of such coating in the

15   oxidized atmosphere is mainly $Al_4B_2O_9$, while the oxidized product becomes $Al_{18}B_4O_{33}$ in relatively higher temperature (>1000°C). Both of these oxidation products are desirable for fiber-reinforced CMCs to form a solid diffusion barrier and protection layer at the interface of the reinforced fibers and matrix. Meanwhile, B_2O_3 (glass) may also form in the liquid phase from the very beginning of the oxidation and acts as a crack/pores sealant

20   to provide additional oxidation-resistance to the reinforced ceramic fibers in this matrix.

The following nonlimiting examples are provided to further illustrate the present invention.

EXAMPLES

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Example 1: Materials

SiC fibers used were Tyranny ZMI fibers produced by Ube Industries, Japan, (~10µm in diameter).

30   **Example 2: Synthesis of Coatings**

Ceramic fibers are coated with BAN coatings comprising 0% BN-Al(O)N to 100%Al(O)N0-BN.

(1) Chlorination

The process for synthesis of intermediate carbon films on SiC utilizes a chlorine extraction method. The carbon coatings obtained are conformal and do not change the shape or surface quality of the samples. They have nanoscale porosity, and excellent adherence to SiC.

5   Tyranno ZMI SiC fibers produced by Ube Industries, Japan, (~10μm in diameter) were treated in pure Cl_2 with gas flow of 10sccm for 3 hours at 550°C and 650°C in atmospheric pressure to form carbon coatings on fibers with the thickness of ~ 0.15μm and ~1.5μm, respectively.

10   (2) Infiltration

Boric acid was used as the most economical precursor for the synthesis of BN. Moreover, unlike other precursors, it does not contaminate the samples by introducing metal impurities. A vacuum chamber was used to infiltrate saturated H_3BO_3 solution into the carbon layer formed on the SiC. The reduced pressure in the chamber induced the

15   release of the gases absorbed on the surface of the nanoporous carbon layers, so that better infiltration could be achieved.

The CDC coated fibers were placed in the vacuum infiltration chamber and pumped down for about 30 minutes. They were then infiltrated with saturated H_3BO_3 solution at 100°C. Cold distilled water was used to wash out the excess crystallized

20   H_3BO_3 from the fiber surface at room temperature. To achieve good infiltration effect for the nanoporous carbon coating, this step was repeated two or three times.

(3) Nitridation

Infiltrated CDC-coated SiC fibers were loaded in a quartz holder and put into a

25   horizontal quartz tube furnace. Before each experimental run, the furnace was purged with argon for at least 30 minutes. Then the furnace was heated to the desired operating temperature at a rate of 10°C/min with ammonia (grade 4: purity 99.99%, BOC gases) flowing into the reaction tube at a flow rate of 10sccm. The sample was held at the set temperature for a period of time to secure the completion of the reaction, and then cooled

30   down in the furnace under the ammonia flow for protection. The specific treatment temperatures and times for different SiC samples are shown in Table 1.

Example 3: Studies of Coating Thickness

The coating thickness is examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Example 4: Studies of Coating Composition

The coating composition was studied by using Energy Dispersive Spectroscopy (EDS) in SEM.

Example 5: Determination of Fiber Strength

Fiber strength is determined by tensile testing of single fibers at room temperature. Changes in Young's modulus and strength after coating as well as interfacial sliding are used as parameters of strength after coating. The coated fibers were compared with untreated fibers by conducting tensile tests for single fibers according to ASTM 3375-79. 10 to 20 fibers were tested for each sample. Room temperature tests were performed with a gauge length of 25 mm using paper frame holders. The average value of the diameter of each kind of fiber was determined by SEM images.

Example 6: Oxidation Testing

Oxidation tests are performed on single fibers followed by analysis of cross-section changes and tensile strength measurement.